CESIUM REMOVAL FLOW STUDIES USING ION EXCHANGE

D. D. Lee, J. F. Walker, Jr, and P. A. Taylor
Oak Ridge National Laboratory,*
and
D. W. Hendrickson,**
SGN Eurisys Services Corp.

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INTRODUCTION

Cesium and strontium radionuclides are a small fraction of the mainly sodium and potassium salts in underground storage tank supernatants at U.S. Department of Energy (DOE) sites at Hanford, Oak Ridge, Savannah River, and Idaho that DOE must remediate. Cesium-137 (^{137}Cs) is the primary gamma radiation source in the dissolved tank waste at these sites, and its removal from the supernatant can reduce the hazard and waste classification of the treated waste reducing the further treatment and disposal costs.¹ Several cesium removal sorbents have been developed by private industry and the U.S. DOE's Office of Science and Technology. Several of these removal technologies have been previously tested in small batch and column tests using simulated and a few actual supernatants under DOE's Environmental Management (EM) programs including the Tanks Focus Area (TFA) and the Efficient Separations and Processing (ESP) Cross-Cutting Program.

The most promising technologies have now been tested using actual supernatant in both ORNL and Hanford hot cells using flow systems of a scale suitable to obtain engineering data that has been applied to the design of pilot scale equipment. The Oak Ridge National Laboratory (ORNL) hot cell tests provided direct input to the Cesium Removal Demonstration Project (CsRD) for sorbent selection. The engineered form of crystalline silicotitanate (CST's) was recommended for the project based on the highest column volumes (CV) at 50% breakthrough, best test-to-test consistency, and the fewest operational difficulties using the Melton Valley Storage Tank (MVST) W-27 supernatant. The CsRD at ORNL is now treating up to 94,000 L of MVST supernatant from tank W-29 (which was recently transferred from W-27) using the CST's. As part of the support to

the CsRD, the ORNL hot cell tests also helped select the supernatant for the CsRD, performed the qualification tests for the supernatant and sorbent, generated ^{137}Cs loaded CST sorbent for waste acceptance criteria testing using the Toxicity Characteristic Leaching Procedure (TCLP) and for waste-form development testing, and provided operational experience.

EXPERIMENTAL SYSTEMS AND APPARATUS

This paper describes the research undertaken to design and operate the experimental units constructed to test cesium removal technologies during continuous operation on actual supernatants. In addition, the design and preparations for the operation of the CsRD are discussed.

ORNL

The equipment diagram for the ORNL hot cell continuous-flow system, which is shown in Fig. 1, consists of the tanks, pumps, tubing and fittings, filters, and instrumentation for testing cesium removal. The system has provided a test bed for investigating new technologies, such as 3M's, and complements other DOE-EM supernatant tasks by using larger engineering-scale, continuous equipment to verify and expand previous batch studies. The operation of both small (1-1.5 cm ID), continuous-flow columns and demonstration-scale columns (30.5 cm ID) will also be evaluated, compared, and contrasted. The ESP and TFA will utilize the information from these studies to transfer the technologies being developed to the end user.

The tests reported here give direct comparisons of cesium removal operations conducted in the experimental systems. At ORNL, a large, sixty-liter, batch of MVST supernatant from Tank W-27 was obtained in April, 1995, so that the supplied sorbents could be evaluated using the same feed, which was initially proposed for the CsRD. Several sorbents were then reevaluated at altered feed

conditions and different flow rates as appropriate to test the sorption kinetics. The sorbent materials were tested at a scale that passed from 0.1 to 12 L of supernatant at a prescribed flow rate continuously through the column until the ^{137}Cs concentration in the column effluent reached the desired end point. The progress was followed using an in-line gamma detector and with samples obtained using a fraction collector. Depending on the sorbent being tested, this required from 15 to more than 1200 CV of supernatant to pass through the columns.

The experimental equipment for the ORNL cesium removal project in hot cell C of Building 4501, the procedures used during the experiment, and results of earlier experiments were described previously.² Installation of the experimental equipment in the hot cell, development of the procedures used, and several sorbent tests were completed in FY95-96. During tests, the system is operated continuously with in-line monitoring of the column effluent to detect ^{137}Cs breakthroughs from the sorbent in the module. The monitor is a sodium iodide detector in a lead-shielded container connected to a power supply, amplifier, and Nuclear Data multichannel analyzer system outside the cell. The column effluent passes by the detector head inside a 6.4-mm-OD by 4.8-mm-ID polyethylene tube that has 5 cm of tubing exposed to the detector head. Flow passes through enough tubing, including the filter system, to ensure that at least 30 min has elapsed between liquid leaving the column and entering the gamma detector. That allows any barium-137m, the gamma emitting decay product of ^{137}Cs , that is present in the feed or in the column to decay (thirty minutes is over ten half lives for the 2.5 minute half-life $^{137\text{m}}\text{Ba}$) so that only the cesium that passes through the column is detected by the gamma detector. The detector configuration allows detection of levels of ^{137}Cs of 5 to 10 counts/s above background. The ^{137}Cs level in the feed for the detector is about 7000-12,000 counts/s; thus, the detection limit is about 0.05-0.15% of the feed. The counts for the area of the peak

for ^{137}Cs were monitored, and the total counts for the selected counting times were recorded by the multichannel analyzer program for later printout.

Once loaded, the column was removed from the experimental system and taken from the cell to measure the quantity of ^{137}Cs loaded. The columns are counted using an Aptec intrinsic germanium detector with a Nuclear Data multichannel analyzer system. This system allows the columns to be placed at distances up to several meters from the detector head for counting, which is necessary for materials that load a high level of radioactive cesium. The column product stream is collected in the fraction collector, and samples of these fractions are counted using an LKB Wallac 1282 Compugamma Universal Gamma Counter. The detection limit for this counter is also about 0.1% of the feed concentration. Some sorbent eluent samples contained too much ^{137}Cs for this detector, so they were counted on the Aptec system at 30 cm from the detector head. Some of the fractions that contain solids, or are suspected to contain solids, were sampled through 0.2- μm syringe filters.

The W-27 supernatant used has many similarities to supernatants in tanks at other DOE sites and provided a common basis to test different sorbents for their ability to remove cesium from actual radioactive storage tank supernatant. In the ORNL system, the sorbents were tested using one 1.5 x 15-cm column containing about 10-12 cm^3 of sorbent at flowrates of 3-9 CV per hour. Other sorbent containing apparatus such as the 3M WEB were also easily connected to the system. Sorbents that could be eluted and regenerated were cycled in place through loading, elution, and regeneration. Sorbents were also analyzed by removing the columns from the cell and counting them on a gamma-spectrometer to determine the total loading and/or the efficiency of elution.

The MVST W-27 supernatant used for the cesium absorber tests came from the tank at pH 7.4, but it was adjusted to the pH levels in other tanks (about pH 12.5-13.3) by adding sodium

hydroxide pellets. The supernatant was then settled and filtered. Analyses showed that the original supernatant contained about 3.2×10^5 Bq $^{137}\text{Cs}/\text{mL}$, 7.1×10^{-6} M total Cs, 0.26 M potassium, 4.7 M sodium, and 5.2 M nitrate. For tests to simulate some conditions at other DOE sites, the pH was increased to 14 with sodium hydroxide pellets; additional cold cesium nitrate was also added to give a total cesium concentration seven to ten times the original concentration. After these adjustments, it contained approximately 3.4×10^5 Bq $^{137}\text{Cs}/\text{mL}$, 1.0×10^{-5} M total Cs, 0.31 M potassium, and 5.52 M sodium and with added cesium had 7.5×10^{-5} M total Cs. The ^{137}Cs in MVST supernatants is one to two orders of magnitude less than that contained in some Hanford tank supernatants. The cesium level with cold cesium added approximates the values for Hanford tanks 101-SY and 103-SY (7×10^{-5} M) and also to the double-shell slurry feed (DSSF) simulant. The high cesium feed has a sodium to cesium molar ratio of about 74,000 and a sodium to potassium ratio of 18.

The supernatant chosen for the CsRD was prepared by adding 50% caustic solution to tank W-27, settling for 2 weeks, and then pumping approximately 83,000 L to tank W-29 to mix with the supernatant heel still present after previous operations with W-29. The mixed W-29 was settled for 1 month, and then sampled for the CsRD qualification tests. The W-29 supernatant contained 4.15 M sodium, 0.38 M potassium, 4.6×10^5 Bq $^{137}\text{Cs}/\text{mL}$, 4.3×10^{-6} M total Cs, 4.0 M nitrate, 0.44 M nitrite and a pH of 12.68. Approximately 500 gal of W-29 supernatant was pumped to the CsRD for the first test, which started on September 15, 1996. Measured compositions of all three supernatants used in the column tests in the ORNL hot cell are given in Table 1.

Hanford

The Hanford Site's Tank Waste Remediation System (TWRS) organization requested column-flow tests be performed using selected sorbents with actual Hanford tank supernatant to

verify the applicability of simulant data. Such tests may also identify as of yet unknown problems or interferences when processing actual wastes under actual conditions.³ The Hanford hot cell test apparatus is shown in Fig. 2 and was described in the test report.⁴ The test system consists of two sets of test and guard columns, valves, tubing, and a peristaltic pump all attached to a base and backplate. The columns are 1 cm ID by 15 cm tall glass with bed retainer, 20 μ m upstream filter and a 10 μ m bed support. Instrumentation includes an in-line gamma-radiation detector to follow the progress of the experiment.

The Hanford test system was designed, built, and the disposable hot cell test apparatus was installed in a hot cell after cold testing and calibration. The equipment was inexpensive, easily loaded into the hot cell, and after use, the spent equipment was sectioned and readily disposed. Both lead columns in each train were filled to a bed height of 10 cm giving a column volume of about 7.85 cm³. The guard columns were filled to about 10 cm and 7 cm on the A and B sides, respectively. A single pump was used to feed the columns sequentially, and the test column was sampled and the column effluent passed through the in-line detector prior to passing through the guard column. The inline gamma detector is of cadmium zinc telluride and was situated 60 minutes down stream of the lead column. The effluent passed the detector within 4.8 mm ID Tygon tubing.

Approximately 4.5 L of DSSF supernatant liquor from Hanford Tank 241-AW-101 were received through the sampling efforts of the TWRS Characterization Project at Hanford. One batch of the tank waste was diluted with water to the target concentration of 5 M sodium and processed through the "A" side of the test assembly, through Resorcinol-Formaldehyde (RF) resin in the primary and guard columns. Eight batches of the tank waste were similarly diluted with water and processed

through the "B" side of the test assembly contacting the CST in both the primary and guard columns. Analysis of the Hanford feed is shown in Table 2.

The sorbents were tested during treatment of diluted DSSF supernatant to greater than 50% ^{137}Cs breakthrough. The breakthrough was followed by in-line gamma spectroscopy, and this allowed adjustment of the sampling routine when breakthrough was sooner than originally expected.

Samples of the feeds and column effluents were removed from the cell and submitted for analysis. When the experiment was complete, the RF resin was contacted by 9 CV of 0.5 *M* nitric acid followed by 5 CV of distilled water. It was then removed from the column and digested with 3 *M* nitric acid for disposal. The CST sorbent was dissolved in hydrofluoric and hydrochloric acid and diluted with water to allow for further analytical testing and disposal.

SORBENTS TESTED

These studies tested the most promising cesium sorbents as recommended by the ESP and TFA, based on previous batch tests that screened many sorbents at Hanford,^{5,6} Sandia,^{7,8} Los Alamos,⁹ Savannah River,¹⁰ and Oak Ridge^{11,12}. SuperLig®644C, batch 3695-GM1121, is a polymer resin of the covalently bound SuperLig® macrocycle family of sequestering ligands from IBC Advanced Technologies (American Fork, Utah) and was supplied by Lane Bray of Pacific Northwest National Laboratory (PNNL). The RF resin developed at the Westinghouse Savannah River Company (WSRC) was made in several batches by Boulder Scientific (Mead, Colorado). One batch was supplied directly by Jane Bibler of WSRC (Bibler batch). A second batch was transferred from Jane Bibler to R. R. Brunson and W. D. Bond of the Radiochemical Engineering Development Center (REDC) at ORNL (REDC batch).¹³ A third batch of RF resin was furnished by AEA from batch

BSC-187 supplied by Jane Bibler to AEA (AEA batch). The engineered forms of the crystalline silicotitanate developed by Sandia National Laboratories/Texas A&M were produced and supplied by UOP as IONSIV® IE-911 Lot Nos. 07398-38B and 999096810001. The 3M SLIG 644 WWL WEB with SuperLig®644 embedded was supplied by the 3M New Products Department. The granular potassium cobalt hexacyanoferrate (KCoFeC), lot number JW-40-021, was made and supplied by Eichrome. The CST used in the CsRD qualification test was purchased by ORNL from UOP as IONSIV® IE-911 Lot No. 999096810003 for use in the CsRD operations. It was pretreated by the CsRD personnel in the CsRD cold test loop, following UOP directions and was delivered in slurry form to the hot cell for the small-scale tests.

At Hanford, the sorbents used included RF resin (REDC batch). It was prepared by treating with 10 column volumes (CV) of 0.5 M HNO₃, rinsed with 10 CV of deionized water, and conditioned with 10 CV of 2.5 M NaOH. The CST was provided by UOP, from the Chickasaw, AL, molecular sieve plant as IONSIV® IE-911, lot No. 999096810001, the same batch used in some of the ORNL studies. It was prepared, in batch mode, by wetting the sorbent and removing the fines. A pretreatment step to adjust the pH of the sorbent to be in equilibrium with the waste solution was completed in batch mode with sodium hydroxide, and then the CST was slurried into the test columns and allowed to settle.

EXPERIMENTAL RESULTS

ORNL

A summary of the test results for the sorbent materials tested in the ORNL hot cell flow system is shown in Figs. 3 and 4, and described below. A sample of 3M SLIG 644 WWL WEB

material was contained in a Gelman 25-mm in-line stainless steel filter holder with filter volume (FV) of 1.29 mL. The apparatus was loaded at 1 mL/min (49.78 FV/h) in an upflow through one loading/elution/regeneration cycle. Brown color left the WEB filter for several FV after the supernatant feed began. Loading was 65 FV to 50% breakthrough. The filter was eluted with 0.5 *N* HNO₃ and regenerated with caustic solution.

EICHRON KCoFeC granular sorbent (7.272 g) was loaded at 9 CV/h using W-27 supernatant at pH 13.32. Normally, KCoFeC is stable at pH's below 12-12.5 and is not used above that pH, but was tested for completeness. Normal column operation with low cesium breakthrough continued for over 250 CV. Then the sorbent began to disintegrate, and the cesium level in the effluent rose rapidly and could not be filtered out using 0.2- μ m filters.

SuperLig® 644C was run at 6 CV/h using 3.779 g of dry resin (11.2 mL volume) using W-27 supernatant at pH 13.3. A considerable amount of color left with the initial few CV of feed through the column. After the breakthrough had reached 50% at about 100 CV, the loaded cesium was eluted with 0.5 *N* HNO₃ at a 3 CV/h. Colored liquid also accompanied the first few CV of acid. The elution curve was very sharp and was 95% complete in 6 CV. The resin has a very low density and could be compressed easily (30% or greater), so calculations were adjusted for the smaller column volume due to compression, giving a revised 50% breakthrough of about 138 CV.

SuperLig® 644C was also tested with pH 14.0 W-27 using a special device, developed by J. L. Collins, to keep the bed compact during the volume changes from loading, elution and regeneration. Loading was at 3.5 CV/h, and the elution used 0.5 *N* HNO₃ while the bed was regenerated with 2 *N* NaOH. The first cycle had a total cesium concentration of 1.1×10^{-5} *M* in the feed, and the following three had 7.5×10^{-5} *M* cesium. The bed volume changed by up to 40-50%

when switching from feed to DI water to acid and then caustic and feed. The first loading had 50% breakthrough at about 167 CV. Elution was complete in about 6 CV of 0.5 *N* HNO₃. The next three loadings (high Cs) had 50% breakthroughs occurred at 77, 65, and 50 CV respectively while initial breakthrough of the cesium was less than 10 CV for all three. Two of the loading curves were approximately parallel to the first curve, while the fourth was completely different. Color was seen at the start of each loading, and at each regeneration.

RF resin (Bibler batch) was prepared and used in three tests with W-27 supernatant at pH 13.3. At 7 CV/h 50% breakthrough of cesium occurred at 45 CV. At 2.9 CV/h, the 50% breakthrough was at 36 CV and the shape of the curve was similar to, but steeper than, that in the 7 CV/h RF run. In the third test, RF resin was loaded, eluted, regenerated, and then rinsed five times at 6.0 CV/h. During each cycle, for the first 3-4 CV of feed or regenerant through the bed, brown-colored liquid exited the bed. The 50% breakthroughs were consistent at about 45 to 50 CV, but some operational problems began to develop during the last two loadings. Elution was completed with 0.5 *M* HNO₃ at about 3 CV/h, and the resin volume shrank from about 10 cm³ to about 5.5 cm³ during each elution. Approximately 9-12 CV were required for cesium elution to be essentially complete (>95% cesium removal from the resin).

RF resin (REDC batch) was also loaded with pH 14.0 W-27 supernatant feed containing 1×10^{-5} *M* cesium at 3.5 CV/h to 70 % breakthrough. The Collins device described above was also used during this test. Cesium initially broke through at 7 CV and then the curve was very steep to 50 % at about 18 CV. The elution was with 0.5 *N* HNO₃. A sample of this batch of RF was transferred to Hanford for use in the Hanford test with the DSSF feed and had a 50% breakthrough at 14 CV.

A third RF resin (AEA Batch) was loaded with the pH 13.3 W-27 at a feed rate of 6 CV/h. The loading was continued through 75 CV with the breakthrough only reaching about 1.1-1.2 %. The loading curve shows that the initial breakthrough did not occur until 15 CV and then the curve was very shallow to 1 % at about 65 CV. The brown color in the effluent was also seen.

CST from UOP, IONSIV IE-911 Lot 07398-38B, was first tested at 3 CV/h in downflow using pH 13.3 W-27 supernatant for a total of over 435 column volumes. No problems that could be attributed to the ion exchanger occurred during the continuous run of more than 6 days (24 h/day). The 1% breakthrough came after 100 CV, 10% breakthrough at about 190 CV, and 50% breakthrough at 350 CV. At 6 CV/h loading, the 50% breakthrough of cesium was very close to that obtained at 3 CV/h at 340 CV. No difficulties with the system were observed during either loading.

A third sample of the CST-38B (11.873 g and 10.4 cm³ column volume) was loaded at 6 CV/h with W-27 supernatant at pH 14.0 and a cesium concentration of $7.48 \times 10^{-5} M$ to greater than 55% breakthrough. The loading curve was parallel to the previous 6 CV/h curve, as expected, with the 50 % breakthrough occurring at 272 CV (about 79 % of the breakthrough for feed with lower cesium and hydroxide), the 10 % breakthrough at 122 CV, and the 1 % breakthrough at 55 CV. Again, no difficulties were observed during operation.

A column which contained 10.59 g (10.35 cm³) of UOP IONSIV® IE-911 (Lot 999096810001) CST, the production engineered form of the CSTs, from the Alabama UOP plant, and was used in a repeat of the previous run using the pH 14 high cesium ($7.5 \times 10^{-5} M$) feed at 6 CV/h. However, lower cesium concentration feed ($1 \times 10^{-5} M$) was used in the last 150 CV. The sorbent was treated to remove fines (2-3%) because the CST was fairly dusty and the water was milky after first contact. Initial flow stabilization problems caused an erratic startup. Once flow was

stabilized, the breakthrough curve returned to the level of background before starting the normal increase. The 50 % breakthrough was 294 CV, the 10% breakthrough was 127 CV and the 1 % breakthrough was about 61 CV. This was about 3-10% better than the -38 B at the above breakthrough points. Because this CST is about 10 % less dense than the -38 B material the performance per mass of sorbent is roughly 10-20% better. No difficulties with the system were observed during operation, but it was noted that the pH of the supernatant was reduced by the CST as it passed through the column for the first 100 CV. This is important to note if the supernatant contains any soluble aluminum which could precipitate in and on the bed if the pH drops even slightly.

For the CsRD qualification of CST IONSIV IE-91 (Lot 99909681003) and W-29 supernatant, the CST was pretreated to pH 12.6 with caustic and then fluidized to remove fines using a simulant containing 4.5 M NaNO₃ and 0.1 N NaOH. The W-29 supernatant was sampled from the tank in three 7-L bottles and transferred to the test building. One bottle was then placed in the cell and filtered through a 25 μ m filter prior to entering the column. A column with 10.4 cm³ of the treated CST was loaded at 6 CV/h (8.426 gal/h/ft²) for 560 CV with a minor upset at about 50 CV, but the test was completed uneventfully during the next 500 CV. Data for the cesium analyses are plotted in Fig. 5, and give 50% breakthroughs of 503.7 CV to 546.2 CV for ¹³⁷Cs analyses depending on the analytical method. The analyses showed that the CST loaded Ba, Ca, Cs, gross Alpha and Beta, ⁹⁰Sr, uranium, and zinc, but Hg, Cd, ⁹⁹Tc, Cr, ¹⁰⁶Ru, Rb, Ni, Na, K, and Al were not loaded. A comparison of the CST runs with W-27 and W-29 supernatants is shown in Fig. 6. The 45% increase in the CV processed to 50% breakthrough (from 345 for W-27 to 505 for W-29) can be attributed to the lower total cesium and nitrate concentrations of the W-29 supernatant. The plot also shows the previous curves for comparison and indicates that CST has decreasing performance with

increasing nitrate and increasing performance with increasing pH. As shown in Fig. 7, the apparent breakthroughs for uranium, ^{90}Sr , and Pb were 433 CV, 1164 CV, and 3327 CV, respectively. Sorbent from the loaded column was subjected to a modified TCLP procedure and showed no unacceptable values in the leach solution were found.

Hanford

For the Hanford RF test, the feed preparation resulted in a batch of supernatant with no solids observed. The supernatant was fed through the columns at a rate of 4.14 CV/h (10.16 gal/hr/ft²) for 25 CV. The 50% breakthrough occurred very early compared to what was expected based on the earlier batch testing. The 50% breakthrough occurred at about 14 CV of contact, and normalized to a 5 M sodium basis, the 50% breakthrough was 15.8 CV. The loading curve for the run is shown in Fig. 8. Samples of the feed solution, effluent, eluate and spent resin digest were analyzed. These data provide no conclusive evidence of any retention of the P, S, Cr, Mo, Zn, and Si on the resin. The trace gamma data for ^{134}Cs provides good correlation with the ^{137}Cs data, remaining in linear proportion throughout the test. Trace quantities of alpha emitting isotopes were present in the feed but they were not found at greater than 10% of the feed concentration in the effluents.

Comparison of the in-line gamma counter analysis for ^{137}Cs with the wet radiochemical analysis of fraction samples yielded excellent agreement for both the shape of the curve and for the 50% breakthrough, both yielding 14 CV as shown in Fig. 9. Many of the metals (Ca, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Si, and Zn) that were below the detection limit in the feed and effluent samples were detectable in the eluate from 0.5 M nitric acid elution. The 9 CV of acid elution provided essentially complete elution of the cesium that was retained on the lead column.

Following completion of the RF test, the feed for the CST test was prepared, and feed was started at a desired flowrate of 6 CV/h, with sampling at about 25 CV increments, with total flow of 840 CV. After completion of the feeding, the lines and columns were flushed with caustic solution. This resulted in unanticipated plugging of the beds, presumably due to precipitation of aluminum compounds and blinding of the bed filters when the hydroxide concentration was lowered. After digestion of the sorbent with hydrofluoric and hydrochloric acids, samples of the feed batches, primary column effluents, and guard column effluents, feed solids, and column digests were removed from the cell and analyzed.

The results of the analysis of the CST experiment provided the performance curve shown in Fig. 10. The 50% breakthrough occurred at 696.8 CV, at a feed rate of 6.27 CV/h (15.38 gal/hr/ft²). The various metals in the effluent samples were analyzed and the results showed that most elements did not load on the CST. Comparison of the in-line gamma detection and wet chemistry gamma analysis is shown in Fig. 11. As shown, the methods yielded the same response. Further analyses of the guard column composite samples for the anion and cations showed that ⁶⁰Co, ^{238,239}Pu, and ⁹⁹Tc were detectable primarily because of the large sample volume and the decontamination of the sample by the 2 CST columns.

Following test completion, the system was flushed, and the ion exchanger columns were removed from the test assembly. There was no significant profile of activity over the column length. The sorbent was removed from the columns, and dissolved in hydrofluoric and hydrochloric acid; aliquots were diluted with water and removed from the cell for analysis.

DISCUSSION

Recently, cesium sorbent studies in actual and simulated alkaline waste matrices were completed using powdered and developmental engineered CST materials at the PNNL,^{14,15} ORNL,^{12,16} and Sandia National Laboratories. In addition, a large body of cesium ion exchange data has been collected for the RF resin in simulated and actual waste matrices.^{6,16,17,18,19} Furthermore, the chemical and radiation stability of several organic ion exchange resins has been investigated by numerous researchers.¹⁷⁻²⁰

A small-scale laboratory batch contact experiment evaluating several ion exchange materials for the removal of cesium from simulated and actual Hanford alkaline supernatant has been described.¹⁵ Cesium batch distribution ratios ($K_d = (C_i - C_f)/C_f * V/M$ where C_i is the initial ion concentration in the feed solution, C_f is the final concentration, V is the solution volume in mL, and M is the exchanger mass in grams), column distribution ratios ($\lambda = K_d \times \rho_b$, where ρ_b is the sorbent dry bulk density), and decontamination factors (DF) were compared as a function of solution composition, supernatant to exchanger phase ratio, and multiple sequential contacts. Equilibrium results for the RF showed a range of λ 's from 100 to 2000, depending on the sodium concentration at the same sodium/cesium ratio. Over the same range, the CST-38B λ 's ranged from 1000 to >20,000. When the exchanger results were compared with those using actual waste, the greatest deviation in performance was noted for the RF resin, which had about 25 to 50% lower values across the range, and for the CST-38B at the highest sodium/cesium ratios, which had a 35% drop in performance (although all exchangers showed decreased performance). Most of the ORNL RF column experiments resulted in 50% breakthroughs at CV 2-5 times lower than expected; this reduced performance was probably due to resin degradation during storage. The comparable

experiments using the RF resin supplied by AEA showed 50% breakthrough predictions of greater than 100 CV with the same W-27 used earlier, this result adds credence to degradation being the cause of the poor performance.

In the tests using actual DSSF waste, the test waste was a volume composite from tanks 1101-AW (70%), 106-AP (20%), and 102-AP (10%) diluted to 4.96 ± 0.19 M sodium and 0.478 ± 0.012 M potassium with an initial Na/Cs ratio of 78,000. Under these conditions, the batch distribution ratios obtained with the CST and RF materials predicted approximately 700 and 65 CV, respectively. These data compare favorably to the current column test results of 696 CV for the CST IE-911 but not for the RF resin. The RF differences between the current experiments and the previous batch tests suggest the difference is related to the chemical stability of the resin and prior degradation during storage since very similar results were obtained with the same resin in the two separate tests at ORNL and PNNL.¹⁸⁻²⁰

Poor performance can also be caused by the effects of the resin or particle density during column testing that may not be seen during small batch tests. If the resin is very light, the possibility exists for the resin to almost float and result in an unpacked column, which resembles a fluidized bed in its removal capabilities. This can result in very early breakthrough of the cesium due to the dispersion through the bed. Indications of density and bed height effects were seen with RF resin in several experiments and modeling efforts.²¹ It was shown that in the case of RF resin, a bed length to diameter ratio of 15 was required before the bed actually behaved like a fixed bed with a constant pattern. The Hanford RF column had a height-to-diameter ratio of 10, and the ORNL column had a ratio of 4. As a result, a weighted bed follower, described earlier, was successfully used for the ORNL RF and SuperLig® 644C loading and elution at pH 14 conditions. Other possibilities for poor

breakthrough curves for the RF resins are improper preconditioning of the bed and mismatching of bed presaturant and the column feed, both in salt concentration and in density. Some of these conditions could have had an effect on the runs with W-27 for the organic resins because in some cases they were washed with water before the W-27 feed (5 M salt) began.

Comparison of the ORNL column data for all sorbents used with the W-27 feed to data obtained using simulant and actual supernatants at other sites showed good agreement and predictability from batch equilibrium to column testing except for RF resin, which varied greatly from batch to batch. Further comparisons must take into account not only cesium concentrations, but the pH, the other anions and cations in the supernatant, and the ratios of other cations to the cesium concentration.

These comparative evaluations helped provide critical data for the selection of the sorbent for the CsRD as well as data applicable to other DOE sites. In addition to the cesium removal capacity of the materials tested, the operational characteristics during continuous loading experiments were monitored. The organic sorbents, RF and SuperLig® 644C, and the 3M SLIG 644 WWL WEB material, produced colored products upon the first introduction of feed or during regeneration after elution. They also exhibited volume changes during various stages of the preparation, loading, elution, and regeneration. Some of the experiments produced solids in the effluent that collected in the equipment downstream from the column or module. The high pH of the feed supernatant to the EICHRON KCoFeC resulted in its chemical breakdown and loss in the column effluent. No operational problems were noted for the CST's although preparation of the commercial forms required equilibration with caustic solution and fluidization to remove fines..

As shown with ORNL and Hanford supernatants, the CST materials performed better overall than any of the other materials at all conditions tested. The best kinetic performance occurred at 3 CV/h. The CST was also able to maintain the column effluent at less than 1% breakthrough for much longer than the other materials except the RF (AEA batch). This means that the column effluent through the CST columns contained lower levels of cesium (e.g. if C/C_0 is 0.01, then 99% of the cesium is removed from the supernatant) compared to the SuperLig® 644C, which showed breakthrough in less than 10 CV. The last RF run with the AEA batch of RF resin, although not taken to 50% breakthrough, showed much improved capacity over the two batches of RF that had been previously tested, and the results were closer to those predicted based on the earlier batch contacts.

Comparison of the column data with the W-27 and W-29 feed to the Hanford data with DSSF feed and to data obtained using simulant and actual supernatants in other tests showed good agreement and predictability from batch equilibrium to column testing. There were exceptions, and the comparisons must take into account the cesium concentration, the hydroxide concentration, the other anions and cations in the supernatant, the ratios of the other cations to the cesium concentration, and for the RF resin, the degree of degradation during storage.

The comparative evaluation results summarized in Table 3, provided critical data for the selection of the sorbent for the CsRD. The experiments also provided qualification of the sorbent chosen with the supernatant used, as well as provided data applicable to other DOE sites, taking into account variations and differences in the supernatant compositions. In addition to the cesium removal capacity of the materials tested, the operational characteristics during continuous loading experiments were monitored.

THE CESIUM REMOVAL DEMONSTRATION PROJECT

The Cesium Removal Demonstration Project addresses the fundamental need to selectively remove cesium from the bulk supernatant and concentrate it into a small-volume, stable waste form. The CsRD effort supports enhancement to baseline waste processing efforts at ORNL and Hanford, and offers an alternative at Savannah River. The objectives of the project were:

- Provide full-scale operating data with demonstrated ESP developed sorbent.
- Evaluate the use of mobile, modular equipment for the treatment of high-activity waste.
- Evaluate decontamination methods for hands-on maintenance.
- Provide data to show the relationship between bench-scale and full-scale performance.
- Provide material to Savannah River Site for a vitrification demonstration project.
- Provide a unit for baseline low-level radioactive waste operations at ORNL.

With these objectives, a team was selected to begin the design, development, procurement, and construction of the CsRD. The design alternatives study was completed under the direction of ORNL, and TTI Engineering was chosen to build the mobile, modular CsRD system. Flow diagrams of the system for both sorbent loading with supernatant and sorbent transfer are shown in Fig. 12. The CsRD consists of a 500 gal feed tank and a filter column followed by two ion exchange columns that can be operated separately or in series. The sorbent is slurried into columns before a test is started, and then it is removed as a slurry to a drying drum for final dewatering before shipment.

After the tests described above, UOP was contracted to provide the CST batch for the initial demonstration using up to 94,000 L of MVST supernatant. Once the CsRD system was delivered, ORNL personnel installed the modular, mobile ion-exchange system in existing facilities to begin the full-scale demonstration based on bench-scale qualification tests performed at ORNL using the same

batch of CST and MVST W-29 supernatant as described above. The bench-scale tests also provided loaded CST sorbent for TCLP leach testing to meet waste acceptance criteria at potential disposal sites.

Major accomplishments for the CsRD as of the end of FY-96 have included placing the contract with TTI-Engineering for CsRD system, completion of the design and design review of the system, construction and installation, cold testing, and completion all necessary documentation with federal and state agencies. Startup with actual radioactive supernatant was completed on schedule and treated the first 2000 L of W-29 supernatant. No column problems were encountered during this initial operation. The end point of this run was to be the loading of approximately 25 Ci Cs-137 on the bed.

During FY-97, up to 94,000 L of MVST supernatant will be processed and the effectiveness of Cs removal evaluated. Another goal is to minimize exposure to operating personnel so that the system can be successfully used in long-term treatment operations. It is also important that the unit be successfully decontaminated to enable hands-on maintenance and transfer to other sites. Some of the cesium loaded CST is being tested as a final waste form, and some is being made into a glass to test effective management methods for the spent ion-exchange material. It is hoped that the CsRD program will open opportunities for industry and universities to participate in the development of improved sorbent and help in modeling of the data comparing bench-scale to full-scale systems. The successful completion of the project will open the door for full-scale treatment at DOE sites.

SUMMARY

Technologies evaluated in these tasks apply to the remediation of tank waste supernatants at most DOE sites, particularly highly alkaline supernatants that contain high concentrations of salts. Separation and concentration of the soluble radionuclides, particularly cesium, would result in a much smaller amount of radioactive waste for disposal or long term storage. The CsRD at ORNL is operating with the UOP CST in treating up to 25,000 gal of MVST supernatant and will be transferred to the site operations personnel at the completion of testing. Removal of the radioactive cesium will also reduce shielding requirements and make downstream handling much easier for removing nitrates and/or any other toxic or hazardous components in the salt solution.

Fig. 1. ORNL Cesium Removal System Flow Diagram

Fig. 2. Hanford Bench-Scale Cesium Exchange Flow and Instrument Diagram

Fig. 3. Comparison of sorbents using MVST W-27 adjusted to pH 13.3

Fig. 4. Comparison of cesium sorbents using MVST W-27 adjusted to pH 14

Fig. 5. Loading Curve for CST (lot -0003) at 6 CV/h (Aug. 12-16, 1096) using Commercial CST and W-29 Feed

Fig. 6. Comparison of the Loadings of the CST (-38B, -0001, and -0003) Materials using W-27 and W-29 Supernatants

Fig. 7. Loading Curves for Cesium, Strontium, Uranium, and Lead using CST -0003 and W-29 Supernatant

Fig. 8. Overall Hanford RF test results using In-Line Gamma Detector

Fig. 9. Hanford RF Cesium Removal Results, In-Line vs Wet Gamma Energy Analysis

Fig. 10. In-Line Gamma Detection of CST Treatment Effluent, CV vs C/C₀ at 6 CV/h

Fig. 11. Hanford CST Test In-Line Gamma Detection vs Wet Chemistry

Fig. 12. ORNL CsRD Flow Diagram

RESIN LOADING AND UNLOADING

ORNL DWG 97A-81

Table 1. Analyses of the MVST W-27 and W-29 supernatants

	MVST W-27. pH 13.3	MVST W-27. pH 14.02	MVST W-29 pH 12.68
Radiochemicals	Bq/mL	Bq/mL	Bq/mL
⁶⁰ Co	680	330	500
¹³⁷ Cs	320000	340000	460000
¹³⁴ Cs	1400	920	7600
⁹⁰ Sr	65000	31000	4100
⁹⁹ Tc	270		342
Gross Alpha	0.9	0.4	30
Gross Beta	525000	430000	550000
Cations/anions	mg/L	mg/L	mg/L
Al	0.847	< .146	4.17
As	0.0089	< .0 250	<2.5e-1
Ba	8.04	5.61	0.865
Ca	89.1	3.1	1.42
Cd	0.22	< .11	0.24
Cr	2.96	3.49	3.44
Cs	0.935	9.95	0.58
Cu	<0.0319	0.15	0.07
Hg	0.09	0.117	0.258
K	10300	12000	14700
Na	113000	127000	95400
Ni	1.22	0.73	1.04
Pb	0.0092	< 10	2.89
Rb	1.1	2.06	1.28
Si		29.3	44.1
Sr		26.3	1.65
U	<1.0	0.485	13.3
Zn	0.473	< .148	1.35
Br	288	<50.0	
Cl	3180	2960	3050
NO ₂		2720	20400
NO ₃	322000	298000	250000
SO ₄	1540	1380	15506
TIC, mg/L		300	980
TOC, mg/L		390	500
Density	1.27	1.30	1.233
TDS, mg/L		79000	81000
TS, mg/L		580000	390000
TSS, mg/L		500000	310000
Na/Cs	701451	12764	164483
K/Cs	37446	1206	25345
Total Anion <u>M</u>	5.3897	6.0063	4.4754
Total Cation <u>M</u>	5.1983	5.8320	4.5256
Difference	0.1914	0.1743	-0.0503

Table 2. Analyses of the Diluted Hanford Tank 241-AW-101 Column Feed

Radiochemicals	Feed For RF Columns Bq/mL	Average Feed for CST Columns Bq/mL
⁶⁰ Co	<225	<233
¹³⁷ Cs	8550000	7918000
¹⁵⁴ Eu	<1598	<1602
¹⁵⁵ Eu	<8473	<6586
²⁴¹ Am	<19536	<13764
Cations/anions	mg/L	mg/L
Al	15300	15500
As	<40.1	<40.1
Ag	9.09	8.95
Ba	<20	<20
Ca	<40.1	<40.1
Cd	<2.0	<2.0
Cr	56.9	59.2
Cu	<40.1	<40.1
K	19800	19350
Li	4.36	4.46
Mo	31.8	31.5
Na	126000	126800
Ni	<8.02	<8.02
P	128	151
Pb	<40.1	<40.1
S	223	217
Si	86.6	114
Sr	<4.01	<4.01
U	<200	<200
Zn	9.52	10.1
Zr	7.73	7.62
	(for corrected dilution)	
Br	<267	<267
F	1110	635
Cl	3140	3130
NO ₂	56100	58600
NO ₃	91100	94900
OH	45900	45730
PO ₄	287	525
SO ₄	391	315
TIC, mg/L	862	1380
TOC, mg/L	7400	
Oxalate	245	297
Na/Cs		66600
Total Anion <u>M</u>	5.819	5.886
Total Cation <u>M</u>	6.275	6.258
Difference	0.456	0.371

Table 3. Comparison of sorbent results for ORNL Cell C continuous column cesium removal experiments

Sorbent	MVST W-27 Feed Supernatant	Flow Rates (CV/h)	Loading Cycles	CV to Breakthrough			Comments
				1%	10%	50%	
CS-100	pH 13.3, Cs=7.5 E-6 M	3	1	3,	7,	18	No longer commercial
RF (Bibler-'95)	"	3	1	12,	20,	35	Color/ shrink-swell
RF (Bibler-'95)	"	6	5	4,	11,	40	Color/ operational/
RF (Bibler-'95)	"	7	1	7.5,	17,	48	Color
RF (REDC-Bibler)	pH 14.02, Cs=1 E-5 M	6	1	10,	14,	18	Color
RF (AEA-BSC-187)	W-27, pH 13.3	6	1	65,	140		Color, poor elution
SuperLig® 644C	"	3	1	20,	65		Color, low density, swell/ shrink
SuperLig® 644C	"	6	1	1,	10,	100	"
SuperLig® 644C	pH 14.02, Cs=1 E-5, (1) 7.5E-5 M (3)	3.5	4	15, 4.5, 15, 2,	46, 16, 31, 6,	166 70 70 50	Color, good elution, volume changes poor reproducibility
3M SLC WEB	W-27, pH 13.3	49.8	1	18,	38,	60	Color, Swell, Poor elution
KCoFeC	"	9	1	85,	250,	250	Disintegrates at pH, fines
CST-38B	"	3	1	114,	192,	350	No problems
CST-38B	"	6	1	82,	174,	342	No problems
CST-38B	pH 14.02, Cs=7.5E-5 M	6	1	55,	123,	273	No problems
CST-0001	"	6	1	60,	129,	296	No problems
CST-0003	W-29, pH 12.6, Cs=4.4E-6 M	6	1	100,	226,	505	No problems

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